Rhenium(I) Tricarbonyl Halide Complexes of Pyrazolylbipyridine Ligands. Part 1. Nuclear Magnetic Resonance Studies of Solution Fluxionality

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Pentacarbonylhalogenorhenium(I) complexes reacted with 6-(pyrazol-1-yl)-2,2'-bipyridine (pbipy) to form stable octahedral complexes of type *fac*-[ReX(CO)$_3$(pbipy)] (X = Cl, Br or I) in which pbipy acts as a bidentate chelate ligand. Mono- and di-methyl derivatives of this ligand formed similar series of complexes. In all cases chemically distinct pairs of complexes involving both bipyridyl and pyridyl/pyrazolyl co-ordination were formed but could not be separately isolated. The 'bipyridyl' co-ordinated complexes predominate (> 80%) in solution. These exchange with the pyridyl/pyrazolyl co-ordination species by a 1,4-metallotropic shift, the rates and mechanism of which were followed by variable-temperature NMR spectroscopy. Energy barriers ($\Delta G^\ddagger$) for this process were in the range 66–76 kJ mol^{-1}.

2,2':6',2''-Terpyridine (terpy) binds to many metals in a terdentate manner if a meridional co-ordination geometry is available.[1] However, the facial geometries of metal moieties such as [PtXMe$_3$] or [ReX(CO)$_3$] force the ligand into a bidentate chelating role leaving one of the pyridyl rings unco-ordinated.[2-4] A similar outcome occurs with 2,6-bis(pyrazol-1-yl)pyridine (bppy) where the bidentate bonding now involves pyrazolyl and pyridyl nitrogen donors.[5] This compound consists of a π-deficient six-membered pyridyl ring and two π-excessive five-membered pyrazolyl rings as distinct from the three π-deficient six-membered rings of terpy. Whilst terpy acts in a bidentate manner in complexes with a wide range of metals [*e.g.* Pt^{IV},[2] Re^{I},[3,4] Ru^{II},[6,7] Cr^{0},[6] Mo^{0},[6] W^{0},[6] Pd^{II} (ref. 8) and Pt^{II} (ref. 8)], bppy is known to act in this way only with Re^{I}.[5] This present paper explores the nature of the co-ordination complexes formed with rhenium(I) by unsymmetrical compounds consisting of one pyrazolyl and two pyridyl rings. In particular it focuses on *fac*-[ReX(CO)$_3$L] [X = Cl, Br or I; L = 6-(pyrazol-1-yl)-2,2'-bipyridine (pbipy), 6-(4-methylpyrazol-1-yl)-2,2'-bipyridine (mpbipy), or 6-(3,5-dimethylpyrazol-1-yl)-2,2'-bipyridine (dmpbipy)]. The lower symmetry of the ligands L compared to terpy and bppy provides the possibility for pairs of chemically distinct co-ordination complexes being formed, depending on which adjacent pair of the three chemically different nitrogen donors is involved in co-ordination. An NMR study has been carried out to identify the different co-ordination species and to examine any fluxionality which might lead to their interconversion.

Experimental

Materials.—The compounds [ReX(CO)$_5$] (X = Cl, Br or I) were prepared by previous methods.[9,10] 4-Methylpyrazole was obtained from Janssen Chimica and used without further purification.

Synthesis of Pyrazolylbipyridines.—6-(Pyrazol-1-yl)-2,2'-bipyridine and 6-(3,5-dimethylpyrazol-1-yl)-2,2'-bipyridine were prepared by the addition of 6-chloro-2,2'-bipyridine[11] to the potassium salt of the corresponding pyrazole according to the method previously reported.[12] 6-(4-Methylpyrazol-1-yl)-2,2'-bipyridine was prepared in an analogous manner as described below.

6-(4-*Methylpyrazol*-1-*yl*)-2,2'-*bipyridine*. 6-Chloro-2,2'-bipyridine (2.01 g, 10.58 mmol) was added to a *ca.* 30% excess of potassium 4-methylpyrazolate [prepared from equimolar quantities of 4-methylpyrazole and potassium metal at 70 °C in anhydrous diglyme (2,5,8-trioxanonane) (45 cm^3)], and the resultant mixture stirred at 130 °C for 3 d. The solvent was removed *in vacuo* and the resulting dark brown oil dissolved in 1 mol dm^{-3} hydrochloric acid (50 cm^3); the solution was then made neutral by addition of dilute aqueous sodium hydroxide. Extraction with dichloromethane (3 × 150 cm^3) followed by drying over MgSO$_4$ and removal of the solvent yielded a brown oil. This oil was loaded on to an alumina (neutral activity Brockman grade I) chromatography column; elution with light petroleum (b.p. 40–60 °C) followed by removal of the solvent *in vacuo* gave the product as a white solid (1.94 g) in 78% yield.

Synthesis of Complexes.—All preparations were carried out using standard Schlenk techniques[13] under purified nitrogen using freshly distilled and degassed solvents. The complexes [ReX(CO)$_3$L] (L = pbipy, mpbipy, or dmpbipy; X = Cl, Br or I) were all prepared in a similar manner. The details for [ReBr(CO)$_3$(pbipy)] are given below. Synthetic, analytical and mass spectral data are given in Tables 1 and 2.

Bromotricarbonyl[6-(*pyrazol*-1-*yl*)2,2'-*bipyridine*]-*rhenium*(I). The compound [ReBr(CO)$_5$] (0.4 g, 0.98 mmol) and pbipy (0.42 g, 1.90 mmol) were dissolved in benzene (45 cm^3) and the mixture heated under reflux for 4 h, after which time the solution infrared spectrum showed loss of signals (at 2155, 2047 and 1987 cm^{-1}) attributable to [ReBr(CO)$_5$]. The volume was reduced to ≈15 cm^3 and light petroleum (b.p. 40–60 °C, 70 cm^3) added to precipitate a yellow solid. The almost colourless solvent was decanted and the solid was washed with light petroleum (50 cm^3) and then dried under vacuum. Recrystallization from dichloromethane–hexane gave the desired product as orange crystals. Yield 0.39 g (70%).

Physical Methods.—Hydrogen-1 NMR spectra were recorded in this Department on either a Bruker AM-250 spectrometer operating at 250.13 MHz or an AC-300 spectrometer operating at 300.13 MHz; 400 MHz ^{1}H spectra of [ReBr(CO)$_3$(pbipy)] were recorded on a Bruker DRX-400 spectrometer at the laboratories of Bruker Spectrospin, Coventry. A mixing time of 0.5 s was used for the phase-sensitive two dimensional exchange spectroscopy (EXSY). The selective total correlation spectroscopy (TOCSY) experiments[14,15] used a composite-pulse decoupling in the presence of

Table 1 Synthetic and analytical data for the complexes [ReX(CO)$_3$L] (L = pbipy, mpbipy or dmpbipy; X = Cl, Br or I)

Complex	Yield[a] (%)	$\tilde{\nu}_{CO}$[b]/cm^{-1}	Analysis[c] (%) C	H	N
[ReCl(CO)$_3$(pbipy)]	85	2028vs, 1927s, 1898s	36.1 (36.4)	1.7 (1.9)	10.1 (10.6)
[ReBr(CO)$_3$(pbipy)]	70	2028vs, 1929s, 1901s	32.8 (33.6)	1.7 (1.8)	9.3 (9.8)
[ReI(CO)$_3$(pbipy)]	90	2027vs, 1930s, 1904m	32.1[d] (31.0)	1.6 (1.6)	9.1 (9.0)
[ReCl(CO)$_3$(mpbipy)]	76	2027vs, 1926s, 1898s	35.9 (36.7)	2.1 (2.2)	9.6 (10.1)
[ReBr(CO)$_3$(mpbipy)]	90	2027vs, 1926s, 1899s	35.1 (34.8)	1.9 (2.1)	9.4 (9.6)
[ReI(CO)$_3$(mpbipy)]	97	2026vs, 1928s, 1902s	32.1 (32.2)	2.4 (1.9)	7.4 (8.9)
[ReCl(CO)$_3$(dmpbipy)]	96	2025vs, 1923s, 1896s	38.6 (38.9)	2.5 (2.5)	9.7 (10.1)
[ReBr(CO)$_3$(dmpbipy)]	97	2026vs, 1925s, 1898s	35.9 (36.0)	2.3 (2.4)	8.9 (9.3)
[ReI(CO)$_3$(dmpbipy)]	67	2023vs, 1922s, 1901s[e]	33.0 (33.0)	2.2 (2.2)	7.7 (8.7)

[a] Relative to metal-containing reactant. [b] Recorded in benzene; s = strong, v = very, m = medium. [c] Calculated values in parentheses. [d] A second analysis had a more consistent carbon result but less consistent H and N. [e] Recorded in thf solution.

Table 2 Mass spectral data for the complexes [ReX(CO)$_3$L] (X = Cl, Br or I; L = pbipy, mpbipy or dmpbipy)

Complex	*m/z* $[M]^+$	$[M - CO]^+$ *	$[M - 2CO]^+$	$[M - 3CO]^+$ *	$[M - 3CO - X]^+$	$[L]^+$
[ReCl(CO)$_3$(pbipy)]	528	500	472	444	409	222
[ReBr(CO)$_3$(pbipy)]	572	544	516	488	409	222
[ReI(CO)$_3$(pbipy)]	620	592	564	536	409	222
[ReCl(CO)$_3$(mpbipy)]	542	514	486	458	422	236
[ReBr(CO)$_3$(mpbipy)]	586	558	530	502	422	236
[ReI(CO)$_3$(mpbipy)]	634	606	578	554	422	236
[ReCl(CO)$_3$(dmpbipy)]	556	528	500	472	436	250
[ReBr(CO)$_3$(dmpbipy)]	600	572	544	516	436	250
[ReI(CO)$_3$(dmpbipy)]	648	620	592	564	436	250

* Most abundant.

scalar interactions (DIPSI-2) sequence for spin-lock and shaped pulse-selective excitation. All spectra were recorded in CD_2Cl_2, $CDCl_3$ or $CDCl_2CDCl_2$ solutions. A standard B-VT 1000 variable-temperature unit was used to control the probe temperature, its calibration being checked periodically against a Comark digital thermometer. The temperatures are considered accurate to ± 1 °C. Rate data were based on bandshape analysis of ^1H NMR spectra using the authors' version of the standard DNMR 3 program.[16] Activation parameters based on experimental rate data were calculated using the THERMO program.[17] Infrared spectra were recorded on a Perkin-Elmer 881 spectrometer calibrated from the signal of polystyrene at 1602 cm^{-1}. Electron-impact mass spectra were obtained on Kratos Profile spectrometer. Elemental analyses were performed by Butterworth Laboratories, Teddington, Middlesex, London.

Results

The nine complexes [ReX(CO)$_3$L] (L = pbipy, mpbipy or dmpbipy; X = Cl, Br or I) were isolated as air-stable orange crystalline solids in generally high yields (Table 1). Their solutions in benzene displayed three strong carbonyl-stretching bands in the infrared spectra (Table 1) indicating a facial metal co-ordination geometry, thereby implying that the ligands were behaving as bidentate chelates. The mass spectra (Table 2) showed peaks with isotope cracking patterns consistent with the molecular ions and ions assignable to loss of the three carbonyls, as well as a peak due to loss of all three carbonyls *and* halogen. The most abundant peaks were those due to either loss of one or all three carbonyls $[M - CO]^+$ or $[M - 3CO]^+$, with the molecular ion peak, $[M^+]$, and that due to loss of two carbonyls, $[M - 2CO]^+$, having relative abundances of *ca.* 30%.

In contrast to one of the pyrazolylpyridine ligand complexes,[5] further heating of any of the present complexes did not yield any terdentate ligand products.

Static NMR Studies.—(*i*) *Free pyrazolylbipyridines.* Before any analysis of the NMR spectra of the rhenium(I) complexes was attempted the ^1H spectra of the three pyrazolylbipyridines pbipy, mpbipy and dmpbipy were analysed. Their 250 MHz ^1H spectra were essentially first order in nature and the parameters are given in Table 3. All the compounds are depicted in their *trans*, *trans* configurations as these are most likely to be preferred in view of the known crystal structures of their closely related analogues terpy and bppy.[18] In these conformations there is a considerable deshielding (Δδ 0.9–1.2) of the 'inner' ring hydrogens, D and G, compared to their 'outer' counterparts B and E. The same trend is evident for the methyls E and G of dmpbipy where the deshielding Δδ is 0.5. Strong evidence for a *trans*, *trans* orientation of the rings comes from a ^1H nuclear Overhauser effect (NOE) difference experiment performed on dmpbipy where a strong NOE effect was detected between H_D and Me_G.

(*ii*) *Complexes* [ReX(CO)$_3$L] (L = *pbipy, mpbipy* or *dmpbipy*). The solution ^1H NMR spectra of all the complexes consisted of two sets of signals, one set very much more intense than the other, indicating the presence of two different co-ordination species, one of which was predominant in solution. Identification of these pairs of species was made primarily from the relative positions of the two highest-frequency signals (at *ca.* δ 9.1 and 8.8). From studies on terpy complexes of rhenium(I)[3] these are assigned to the *ortho* (or 6′-position) hydrogens of the outer pyridyl ring. Co-ordination to most transition metals causes considerable high-frequency shifts of the resonances of such hydrogens,[2,3,6] and since the more intense signal of these high-frequency pairs displays the larger co-ordination shift this implies that the bidentate co-ordination involves both pyridyl rings rather than the pyridyl and pyrazolyl rings. This conclusion is confirmed further by the fact that the relative intensities of the signals of the corresponding hydrogens of the pyrazolyl ring are reversed to that of the pyridyl ring implying that the preferred complex involves an unco-ordinated pyrazolyl ring.

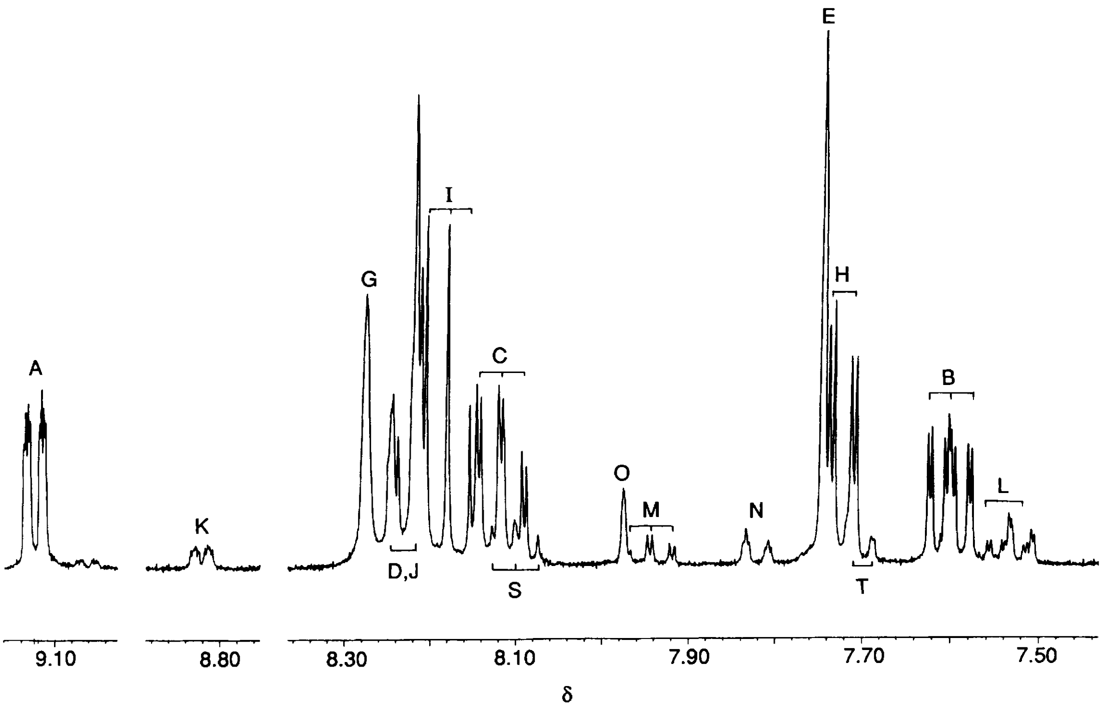


Fig. 1 The 300 MHz ^1H NMR spectrum (aromatic region) of $[ReCl(CO)_3(mpbipy)]$ in $CDCl_3$ at 253 K. For signal labels refer to Table 5

Thus, the complexes exist as pairs of species as depicted in Tables 4–6 where the chemical shift assignments are presented. All ^1H NMR signals of the more abundant complexes were detected and assigned with certainty. This did not prove possible for the less-abundant pyridyl/pyrazolyl co-ordinated complexes due to the weakness of their ^1H signals and numerous partial and complete overlaps of these with the more intense signals. However, near-complete assignments of both complex species were achieved in the cases of $[ReBr(CO)_3(pbipy)]$ (Table 4) and $[ReCl(CO)_3(mpbipy)]$ (Table 5). The latter case will be described in some detail.

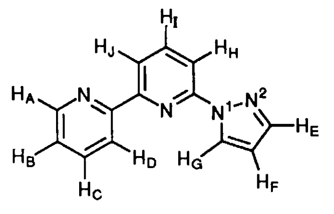
The aromatic portion of the ^1H NMR spectrum of $[ReCl(CO)_3(mpbipy)]$ is shown in Fig. 1. The signals of the co-ordinated pyridyl ring are labelled A–D with H_A (at $\delta \approx 9.1$) displaying a substantial high-frequency co-ordination shift. Signals H_A and H_B are split into eight lines due to spin coupling to the other three hydrogens of this ring. The coupling constants are of very similar magnitude to those of the free pyrazolylbipyridine (Table 3). Signal H_C analyses as a triplet of doublets due to equal coupling to H_B and H_D and weaker coupling to H_A. Owing to the similarity of chemical shifts of H_C and H_D the multiplet structures of these signals show second-order intensity perturbations.[19] The chemical shift of H_D was difficult to define accurately as it is almost identical to that of H_J of the central pyridyl ring. The other hydrogens of this ring H_I and H_H are present as a well defined binomial triplet and 1 : 1 doublet of doublets, respectively. Signals due to H_E and H_G of the pyrazolyl ring are slightly broadened due to unresolved coupling to the CMe groups (Me_F), the relative order of shifts ($\delta_G > \delta_E$) following the trend previously observed for the bppy complexes.[5] The assignments of the weaker set of signals were made on the basis of the expected directions of co-ordination shifts and variable-temperature studies (see later) from which some of the exchanging pairs of signals were identified. Furthermore, the multiplet structures of these weak signals always matched those of their major counterparts. Thus, H_K, H_L, H_M and H_N were assigned as in Table 5. The multiplet structure of H_M (triplet of doublets) overlapped slightly with the singlet of H_O, and that of H_L (doublet of doublet of doublets) overlapped with a weak unknown impurity multiplet. Only signals H_Q and H_R could not be assigned.

The spectra of the other complexes were interpreted in a similar manner, the assignments of $[ReBr(CO)_3(pbipy)]$ being further substantiated by two-dimensional EXSY spectra (see later). An examination of the shift data in Tables 4–6 reveals certain consistent trends both in actual shifts, δ, and, in particular, in the internal co-ordination shifts, Δδ, as defined by $\delta_A - \delta_K$, $\delta_B - \delta_L$, *etc.* Such shifts were rather more informative than the usual co-ordination shifts measured relative to free-ligand shift values.[5] The large co-ordination shifts $\delta_A - \delta_K$ fell in the range 0.28–0.35 and these helped to identify the favoured co-ordination species in solution. The other pyridyl hydrogens H_B, H_C and H_D also experienced high-frequency shifts on co-ordination (*i.e.* their Δδ values were positive). Hydrogen H_J on the central pyridyl ring exhibited a particularly large high-frequency shift which was attributed in large measure to the rotation of the outer pyridyl ring from a *trans* to a *cis* orientation on co-ordination.[5] In contrast, the parameters $\delta_E - \delta_O$ and $\delta_G - \delta_Q$ were negative for these pyrazolyl ring hydrogens since δ_O and δ_Q refer to *co-ordinated* pyrazolyl rings. The parameter $\delta_F - \delta_P$ is also negative (−0.08 to −0.12) for CH shifts (*e.g.* pbipy complexes) but is approximately zero for CMe shifts (*e.g.* mpbipy complexes).

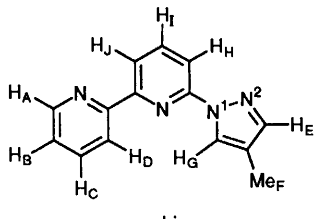
Dynamic NMR Studies.—On warming solutions of the complexes their ^1H NMR spectra showed subtle changes indicative of fluxional exchange between the major [bis(pyridyl) co-ordinated] and minor (pyridyl/pyrazolyl co-ordinated) species. In all cases, the exchanging pairs of hydrogens, $H_A \rightleftharpoons H_K$, were clearly identified in the highest-frequency region of the spectrum. In the pbipy complexes the hydrogen pairs $H_F \rightleftharpoons H_P$ were also identified. The exchanges between both these pairs of signals were subsequently submitted to total bandshape analysis (see later). The fluxional exchange in the complex $[ReBr(CO)_3(pbipy)]$ was examined in more detail by both two-dimensional EXSY and one-dimensional bandshape experiments.

The full ^1H NMR spectrum of $[ReBr(CO)_3(pbipy)]$ is shown in Fig. 2 with assignments for all signals except those of H_N and H_T of the minor co-ordination species (see Table 4). Assignments of the signals of the major co-ordination species were straightforwardly achieved, being based on previous experience

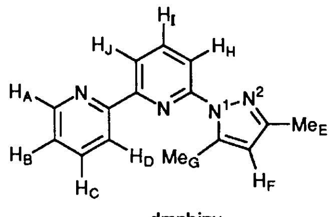
Table 3 Hydrogen-1 NMR data* for the pyrazolylbipyridines in $CDCl_3$ at 303 K



pbipy



mpbipy



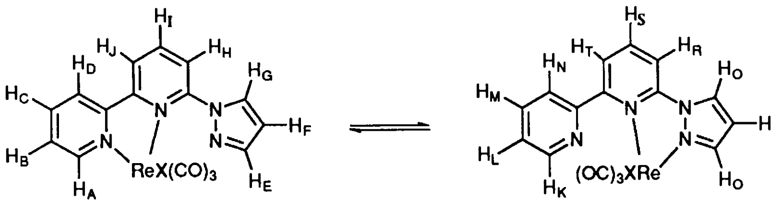
dmpbipy

Compound	δ_A	δ_B	δ_C	δ_D	δ_E	δ_F	δ_G	δ_H	δ_I	δ_J
pbipy	8.27	6.84	7.33	8.00	7.42	6.11	8.32	7.63	7.45	7.96
mpbipy	8.36	6.95	7.45	8.10	7.27	1.88	8.13	7.65	7.54	7.99
dmpbipy	8.59	7.20	7.70	8.24	2.25	6.00	2.70	7.87	7.80	8.24

Compound	$^3J(H_AH_B)$	$^4J(H_AH_C)$	$^5J(H_AH_D)$	$^3J(H_BH_C)$	$^4J(H_BH_D)$	$^3J(H_CH_D)$	$^3J(H_EH_F)$	$^4J(H_EH_G)$	$^3J(H_FH_G)$	$^3J(H_HH_I)$	$^4J(H_HH_J)$	$^3J(H_IH_J)$
pbipy	4.7	1.8	0.9	7.5	1.1	8.0	1.6	0.7	2.6	8.0	0.9	7.7
mpbipy	4.8	1.5	0.8	7.6	~1	7.6	~0	< 1	~0	7.7	~1	7.8
dmpbipy	4.8	1.8	0.9	7.5	1.2	7.8	~0	~0	~0	8.2	1.2	7.4

* Chemical shifts, δ, relative to $SiMe_4$ (δ 0); spin–spin coupling constants, *J*, in Hz.

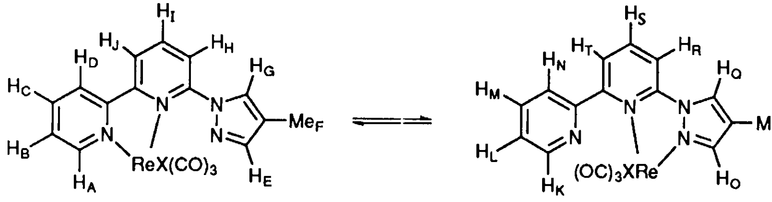
Table 4 Hydrogen-1 NMR data[a] for the complexes $[ReX(CO)_3(pbipy)]$



X	Solvent	*T*/K, Co-ordination shift[b]	$\delta_{A/K}$	$\delta_{B/L}$	$\delta_{C/M}$	$\delta_{D/N}$	$\delta_{E/O}$	$\delta_{F/P}$	$\delta_{G/Q}$	$\delta_{H/R}$	$\delta_{I/S}$	$\delta_{J/T}$
Cl	$CDCl_3$	253	9.14 (A)	7.62 (B)	8.14 (C)	≈8.25 (D)	7.95 (E)	6.67 (F)	8.54 (G)	7.76 (H)	8.23 (I)	≈8.25 (J)
			8.86 (K)	?	?	?	?	6.75 (P)	?	?	?	?
		Δδ	0.28					−0.08				
Br	CD_2Cl_2	273	9.10 (A)	7.59 (B)	8.13 (C)	8.29 (D)	7.91 (E)	6.66 (F)	8.28 (G)	7.68 (H)	8.23 (I)	8.31 (J)
			8.80 (K)	7.52 (L)	7.94 (M)	?	8.11 (O)	6.77 (P)	8.42 (Q)	7.82 (R)	8.17 (S)	?
		Δδ	0.30	0.07	0.19		−0.20	−0.11	−0.14	−0.14	0.06	
I	CD_2Cl_2	253	9.16 (A)	7.60 (B)	8.17 (C)	≈8.3 (D)	7.93 (E)	6.68 (F)	8.34 (G)	7.67 (H)	8.28 (I)	≈8.3 (J)
			8.81 (K)	?	?	?	?	6.80 (P)	?	?	?	?
		Δδ	0.35					−0.12				

[a] Chemical shifts, δ, relative to $SiMe_4$ (δ 0). [b] Internal co-ordination shifts, Δδ ($= \delta_A - \delta_K, \delta_B - \delta_L$, *etc.*).

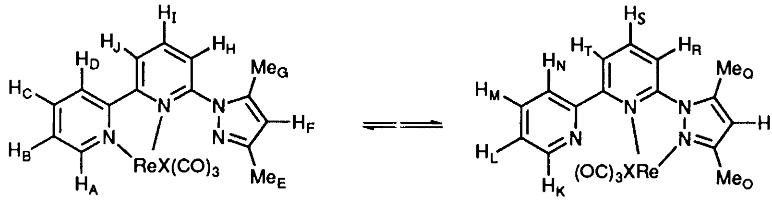
Table 5 Hydrogen-1 NMR data[a] for the complexes [ReX(CO)$_3$(mpbipy)]



X	Solvent	T/K, Co-ordination shift[b]	$\delta_{A/K}$	$d_{B/L}$	$\delta_{C/M}$	$\delta_{D/N}$	$\delta_{E/O}$	$\delta_{F/P}$	$\delta_{G/Q}$	$\delta_{H/R}$	$\delta_{I/S}$	$\delta_{J/T}$
Cl	CDCl$_3$	253	9.12 (A)	7.60 (B)	8.12 (C)	≈8.24 (D)	7.74 (E)	2.20 (F)	8.28 (G)	7.72 (H)	8.18 (I)	≈8.22 (J)
			8.82 (K)	7.54 (L)	7.94 (M)	7.82 (N)	7.98 (O)	≈2.21 (P)	?	?	8.10 (S)	7.70 (T)
		Δδ	0.30	0.06	0.15	0.42	−0.24	≈0			0.08	0.52
Br	CD$_2$Cl$_2$	263	9.12 (A)	7.61 (B)	8.15 (C)	≈8.3 (D)	7.73 (E)	2.19 (F)	7.74 (G)	7.68 (H)	8.23 (I)	≈8.3 (J)
			8.81 (K)	7.54 (L)	7.94 (M)	?	7.99 (O)	≈2.20 (P)	?	?	?	?
		Δδ	0.31	0.07	0.21		−0.26	≈0				
I	CDCl$_3$	253	9.12 (A)	7.55 (B)	8.10 (C)	≈8.25 (D)	7.72 (E)	2.22 (F)	7.85 (G)	7.61 (H)	8.20 (I)	≈8.3 (J)
			8.77 (K)	?	7.92 (M)	?	7.96 (O)	≈2.23 (P)		?		7.67 (T)
		Δδ	0.35		0.18		−0.24	≈0				0.63

[a] Chemical shifts, δ, relative to SiMe$_4$ (δ 0). [b] Internal co-ordination shifts, Δδ (= $\delta_A - \delta_K$, $\delta_B - \delta_L$, *etc.*).

Table 6 Hydrogen-1 NMR data[a] for the complexes [ReX(CO)$_3$(dmpbipy)]



X	Solvent	T/K, Co-ordination shift[b]	$\delta_{A/K}$	$\delta_{B/L}$	$\delta_{C/M}$	$\delta_{D/N}$	$\delta_{E/O}$	$\delta_{F/P}$	$\delta_{G/Q}$	$\delta_{H/R}$	$\delta_{I/S}$	$\delta_{J/T}$
Cl	(CDCl$_2$)$_2$	263	9.07 (A)	7.58 (B)	8.11 (C)	≈8.3 (D)	≈2.3 (E)	6.14 (F)	≈2.3 (G)	7.47 (H)	8.20 (I)	≈8.3 (J)
			8.79 (K)	?	?	?	?	?	?	?	?	?
		Δδ	0.28									
	CDCl$_3$						2.34 (E)		2.37 (G)			
Br	(CDCl$_2$)$_2$	263	9.06 (A)	7.54 (B)	8.08 (C)	≈8.3 (D)	≈2.3 (E)	6.14 (F)	≈2.3 (G)	7.45 (H)	8.18 (I)	≈8.3 (J)
			8.80 (K)	?	?	?	?	?	?	?	?	?
		Δδ	0.26									
	CDCl$_3$						2.32 (E)		2.37 (G)			
I	CDCl$_3$	303	9.21 (A)	7.53 (B)	8.07 (C)	≈8.3 (D)	≈2.3 (E)	6.11 (F)	≈2.3 (G)	7.43 (H)	8.16 (I)	≈8.3 (J)

[a] Chemical shifts, δ, relative to SiMe$_4$ (δ 0). [b] Internal co-ordination shifts, Δδ (= $\delta_A - \delta_K$, $\delta_B - \delta_L$, *etc.*).

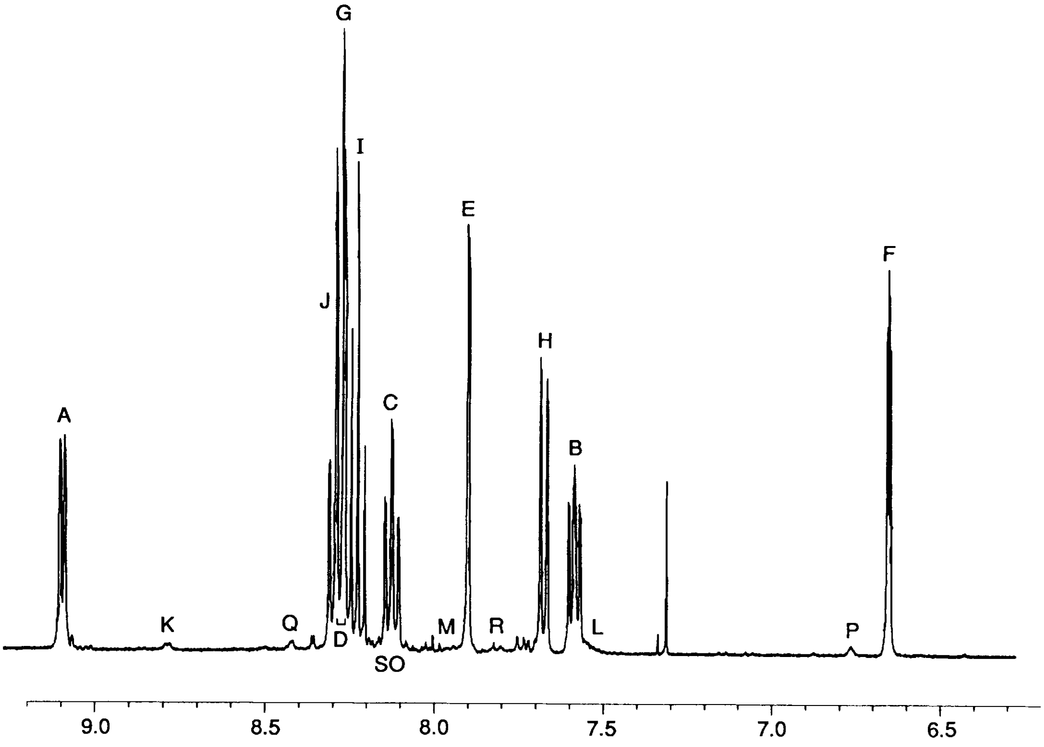


Fig. 2 The 400 MHz ^1H NMR spectrum of $[ReBr(CO)_3(pbipy)]$ in CD_2Cl_2 at 279 K. For signal labels refer to Table 4

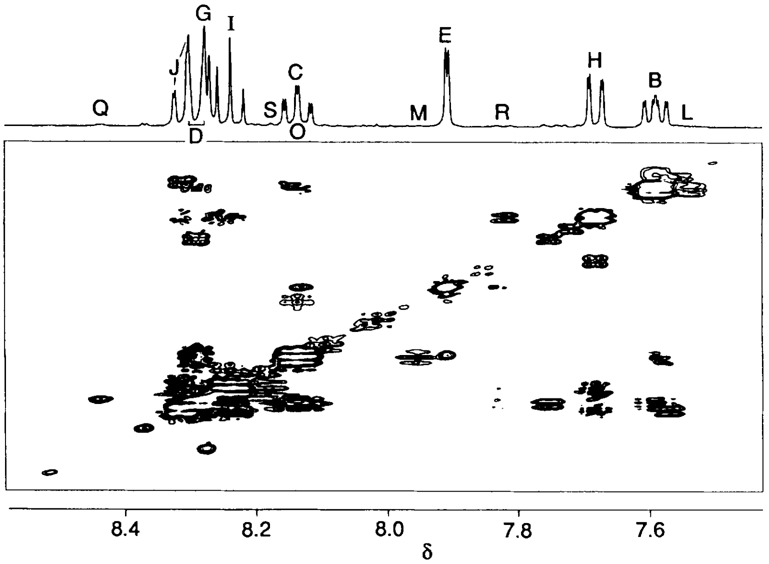


Fig. 3 Portion of the 400 MHz ^1H phase-sensitive two-dimensional EXSY spectrum (mixing time 0.5 s) of $[ReBr(CO)_3(pbipy)]$ in CD_2Cl_2 at 298 K. For signal labels refer to Fig. 2 and Table 4

of terpy[3] and bppy systems,[5] and on selective TOCSY experiments[14,15] which identified the three separate spin systems associated with the three ligand rings. Assignments of the minor signals were based on the identification of exchange cross-peaks in the two-dimensional EXSY spectrum (Fig. 3). Here the exchanging pairs $H_B \rightleftharpoons H_L$, $H_C \rightleftharpoons H_M$, $H_G \rightleftharpoons H_Q$, $H_H \rightleftharpoons H_R$ and $H_I \rightleftharpoons H_S$ can be detected even though in most cases the diagonal signals of the minor signals are absent. This illustrates the 'intensity borrowing' of exchange cross-peaks from both diagonal peaks in two-dimensional EXSY[20] and is a useful assignment aid.

Having obtained conclusive evidence for the existence of the fluxional process attempts were made to measure it as accurately as possible. The exchanging pairs $H_A \rightleftharpoons H_K$ and $H_F \rightleftharpoons H_P$ were chosen for this purpose and their signals fitted using the DNMR 3 program[16] in the approximate temperature range 250–350 K. The case of $[ReBr(CO)_3(pbipy)]$ is illustrated in Fig. 4. It can be seen that on warming the solution the minor signals broaden considerably and virtually vanish near the coalescence temperature (*ca.* 373 K), when the major signals experience slight broadenings. These features were reproduced in the computer-simulated spectra and the 'best-fit' rate constants are shown in Fig. 4. Activation-energy data were calculated for all complexes

Table 7 Activation-energy data[a] for the 1,4 Re–N fluxions in $[ReX(CO)_3L]$ complexes

L	X	Populations[b] (%)	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$\Delta G^\ddagger$(298.15 K)/kJ mol^{-1}
pbipy	Cl	98:2	—	—	—
	Br	96:4	68.2 ± 1.5	−5 ± 5	69.5 ± 0.02
	I	95:5	55.3 ± 1.7[c]	−52 ± 6[c]	70.6 ± 0.01[c]
mpbipy	Cl	90:10	65.1 ± 2.1	−11 ± 7	68.3 ± 0.02
	Br	90:10	71.6 ± 4.0	19 ± 14	66.0 ± 0.2
	I	82:18	74.7 ± 3.8	20 ± 13	68.9 ± 0.01
dmpbipy	Cl	99:1	—	—	—
	Br	98.5:1.5	52.5 ± 3.5[c]	−78 ± 11[c]	75.9 ± 0.2[c]
	I	≈100:0	—	—	—

[a] For major ⟶ minor co-ordination species. Errors are purely statistical in nature, based on least-squares fittings of Eyring plots, and do not take account of errors in measurements of isomer populations and sample temperatures. The true errors are likely to be somewhat larger. [b] Values ±0.5%. [c] Of questionable accuracy (see text).

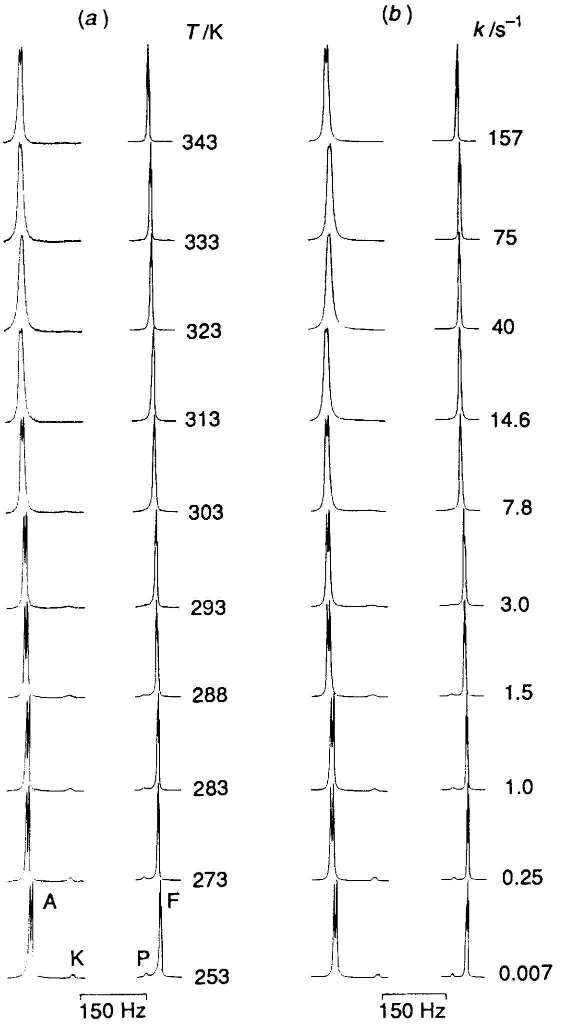


Fig. 4 Experimental (*a*) and computer-simulated (*b*) spectra of portions of the variable-temperature spectra of $[ReBr(CO)_3(pbipy)]$ in $CDCl_2CDCl_2$. 'Best-fit' rate constants for either spectral region are shown alongside

except $[ReCl(CO)_3L]$ (L = pbipy or dmpbipy) where the exceptionally low populations of the minor species prevented meaningful quantitative analysis.

Discussion

The work shows clearly that, when bidentate chelate complexes of pyrazolylbipyridine ligands with the rhenium(I) moiety *fac*-$[ReX(CO)_3]$ are formed, co-ordination involving the nitrogen donors of both pyridyl rings is strongly favoured over that involving nitrogen donors of a pyridyl and pyrazolyl ring. Population ratios in $CDCl_3$ or $(CDCl_2)_2$ solutions are in the range 82:18 to 99:1. Compounds of the 2,2′-bipyridine type are known to co-ordinate with a wide range of metal moieties,[21] whereas pyrazolylbipyridines are far less versatile. Indeed, bppy and its methyl derivatives[5] have been shown to date to act in a bidentate manner in complexes only with Re^I, attempts to isolate complexes of Pt^{IV}, Pt^{II} and Pd^{II} being unsuccessful.[22] The strong preference for bipyridine-type co-ordination complexes in the present work must be related to the more favourable ligand bite angle than that involving a pyridyl plus pyrazolyl ring combination. However, steric and electronic effects in addition to geometric factors appear to be present since methyl substitution on the pyrazolyl ring does alter the populations of the complex species if only marginally. It appears that methyl substitution in the 4 position of the five-membered ring favours the pyridyl/pyrazolyl co-ordinated species slightly whereas 3,5-position substitutions disfavour it somewhat (see Table 7).

The activation energies of the 1,4 Re–N metallotropic shift are given in Table 7. In view of the considerable difficulties in some of the bandshape analyses arising from the gross imbalance of solution populations of the two co-ordinated species, these values need to be examined critically. It must be assumed from previous studies that the fluxion is purely intramolecular in type and therefore activation enthalpies, $\Delta H^\ddagger$, and free energies, $\Delta G^\ddagger$, should be of very comparable magnitude since activation entropies $\Delta S^\ddagger$ should be very small. This, however, is not always the case and despite obtaining very good visual matchings of experimental and computed spectra for the complexes $[ReBr(CO)_3(dmpbipy)]$ and $[ReI(CO)_3(pbipy)]$ we are inclined to disregard these energy values when making wider comparisons with other complexes. Variation of halide, whilst exerting a minor but systematic influence on the solution populations of the co-ordination species, does not appear to have any systematic effect on the activation energies and so averaged values of $\Delta H^\ddagger$ and $\Delta G^\ddagger$ were taken for each ligand and compared with similarly averaged values from our previous work on terpy,[3] bppy,[5] 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (tmbppy),[5] and the single values for 2-(3,5-dimethylpyrazol-1-yl)-6-(pyrazol-1-yl)pyridine (dmbppy).[5] These data are collected in Table 8, where they are given in order of increasing magnitude of the estimated pK_a values of the ligand. Such values are taken as crude measures of the relative donor strengths of the N atoms of these heteroaromatic ligands. Values were estimated from literature pK_a data for pyridine (5.23),[23] pyrazole (2.52),[24] 4-methylpyrazole (3.09)[24] and 3,5-dimethylpyrazole (4.12)[24] by the appropriate combination and averaging of these individual ring values. In view of the variable magnitude in the $\Delta S^\ddagger$ parameter for these complexes it was thought to be more significant in this instance to use $\Delta H^\ddagger$ rather than $\Delta G^\ddagger$ values for comparing activation energies of the fluxional processes. The data in Table 8 show that when this is

Table 8 Activation energies[a] and enthalpies[a] for the 1,4 M–N fluxion in bidentate ligand complexes [$ReX(CO)_3L$] (X = Cl, Br or I)

L	$\Delta G^{\ddagger}$ (298.15 K)/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	Ligand pK_a[b]	Ref.
bppy	55.8	53.0	3.42	5
dmbppy	68.7[c]	64.6[c]	3.96	5
pbipy	69.5[d]	68.2[d]	4.32	This work
tmbppy	73.5	69.8	4.49	5
mpbipy	67.7	70.5	4.52	This work
terpy	71.6	77.8	5.23	3

[a] Averaged values for different halide complexes. [b] Estimated from pK_a values of pyridine, pyrazole, 4-methylpyrazole and 3,5-dimethylpyrazole. [c] Value for [$ReBr(CO)_3$(dmbppy)]. [d] Value for [$ReBr(CO)_3$(pbipy)].

done the relative magnitudes of the activation energies of the fluxional shift (expressed as $\Delta H^{\ddagger}$ values) can be related directly to the donor strengths of the nitrogen pairs (as expressed by estimated ligand pK_a values). Clearly, however, geometric factors such as the change in ligand bite angle on going from the bidentate ligand geometry to the quasi-terdentate geometry of the transition state for the fluxion must also play a role, if only perhaps a minor one.

The mechanism of the fluxion in these pyrazolylbipyridine complexes can be assumed to be of the 'tick-tock' twist type, involving the breaking and making of two Re–N bonds, by analogy with the complexes of bidentate bppy[5] and terpy.[2] Evidence for this mechanism occurring in the present complexes could, in theory, have been obtained from the ^{13}C NMR spectra of the carbonyl signals, where exchange broadening should occur between corresponding equatorial carbonyls. However, in view of the very low intensity of the minor co-ordination species and the difficulty in detecting metal carbonyl signals on account of their long spin–lattice relaxation times, this evidence would be very hard to achieve in practice.

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